DIRECT OBSERVATION OF THE CATALYTIC PRODUCTION OF DIMETHYL CARBONATE USING ON-LINE GC/MS

Brian C. Dunn, Jorg Pahnke, Dan Hopkinson, Edward M. Eyring, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

Genshan Deng, Jacek Dworzanski, Henk L.C. Meuzelaar, Ronald J. Pugmire, Department of Chemical and Fuel Engineering, University of Utah, Salt Lake City, UT 84112.

KEYWORDS: Dimethyl carbonate, fuel oxygenate, on-line GC/MS

INTRODUCTION
Dimethyl carbonate (DMC) has the potential to replace methyl t-butyl ether[1,2] (MTBE) as an oxygenate fuel additive for both diesel and gasoline engines.[3] Previous research has shown that the addition of DMC to gasoline or diesel fuel reduces all forms of emissions: hydrocarbons,[3] carbon monoxide,[4] oxides of nitrogen,[4-6] and particulate matter.[7,8] Numerous routes exist for the production of DMC: reaction of methanol with urea with an organotin catalyst,[9] activation of CO_2,[10-12] and the reaction between methyl nitrite and carbon monoxide.[13] A promising route to the industrial production of DMC is the oxidative carbonylation of methanol.[14,15] A drawback of DMC is the lack of knowledge regarding the reaction mechanism that could lead to the efficient industrial production in sufficient quantity to satisfy the enormous demand in the American fuel market. Discovering the reaction mechanism should allow more efficient catalysts for the production of DMC to be developed and could facilitate the widespread adoption of DMC as an oxygen-containing fuel additive. We are investigating the reaction between methanol, carbon monoxide, and oxygen that produces DMC as one product:

$$2CH_3OH + CO + \frac{1}{2}O_2 \xrightarrow{Cu^{2+}} O = C(OCH_3)_2 + H_2O \qquad (1)$$
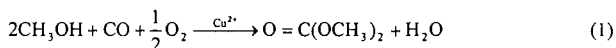
In order to obtain detailed information about the underlying reaction mechanisms and kinetics we are using a novel, on-line GC/MS technique developed at the University of Utah Center for Microanalysis and Reaction Chemistry (UUCMARC) that is capable of repetitively recording GC/MS profiles at 1 minute intervals, or less. This method can be used with a variety of chemical reactors and a broad range of reaction conditions[16-18] and enables definitive identification of many volatile or semi-volatile compounds in relatively complex reaction mixtures, while simultaneously producing kinetic profiles of all compounds as a function of time and temperature.

EXPERIMENTAL
The catalysts are prepared by dissolving the appropriate copper and/or palladium salt in methanol, adding the activated carbon support, and refluxing the mixture with vigorous stirring for four hours. The solvent is removed by vacuum distillation and the catalyst is dried under an inert atmosphere until completely free from solvent.

The reaction is studied by placing a mixture of the reactants and a sample of the previously prepared catalyst into a glass-lined stainless steel autoclave. The reaction chamber is suspended in a preheated fluidized sand bath in which the reaction can be carried out under either isothermal or temperature programmed conditions. The autoclave is interfaced to a GC/MS system that allows on-line identification and monitoring of all of the reaction products in real time and the kinetic profile of the reaction is recorded.

A pressure reduction transfer line and a AVS-GC/MS system, where AVS denotes ambient vapor sampling, have been employed for real-time monitoring of the C1 reaction process by on-line analysis of volatile products from a high pressure batch reactor. The pressure reduction line is a 2 m long, 50 μm i.d. fused silica capillary with a volume flow of 0.8 ml/min as a function of the reaction pressure (the initial pressure: 150 psig, the highest pressure: 350 psig at 170 °C). The vapor sampling and GC functions of the system are contained in the Enviroprobe (FemtoScan Corp.), which attaches to a Hewlett-Packard model 5972 MSD (mass selective detector) via a modified, more power efficient version of the standard GC to MSD transfer line interface. The Enviroprobe utilizes an AVS inlet,[19] which performs the repetitive injection of vapor samples into the 10 m long, 250 μm i.d. fused silica capillary column with the temperature of 80 °C. The sampling time is one second and the sampling interval is two and a half minutes.

RESULTS AND DISCUSION

The on-line GC/MS system was found to perform quite well for this particular reaction process and reactor set-up. Besides providing direct information about the concentrations of organic reactants and products it also proved possible to directly monitor reaction gas components such as oxygen. Since the high partial pressures of these components tend to cause saturation of the molecular ion peak, as well as of the main fragment ion peaks, minor isotope peaks (e.g. $O^{18}O^{16}$ at m/z 34) can be used to monitor the kinetic profiles of these major reaction atmosphere constituents. This proved to be very informative, e.g. by showing that some catalysts cause rapid oxidation of CO to CO_2 at low temperatures, thereby making CO unavailable for the key reaction step with methanol as can be seen from Figure 1.
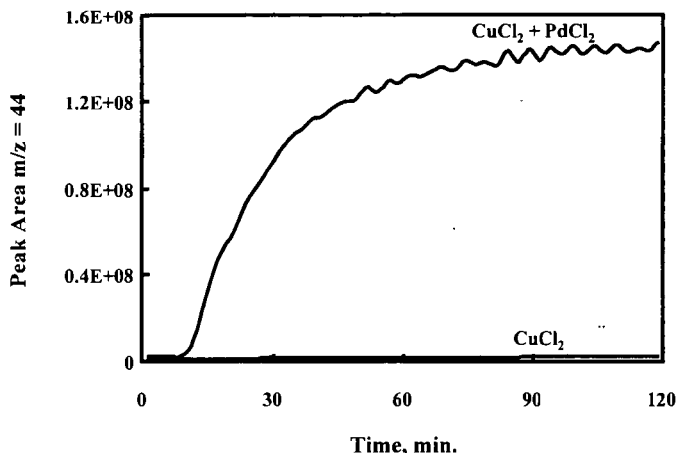

Figure 1. Comparison of CO_2 formation with two different catalysts: $CuCl_2$ + $PdCl_2$ and $CuCl_2$ only.

The effect of catalyst composition on the overall reaction was studied by preparing a series of catalysts using different metal salts. Six catalysts were prepared: $CuCl_2$, $Cu(Ac)_2$ (copper(II) acetate), $Cu(NO_3)_2$, $CuCl_2$ + $PdCl_2$, $Cu(Ac)_2$ + $Pd(Ac)_2$, and $CuCl$. The reactions were conducted under temperature-programmed conditions from 100 °C to 170 °C in order to observe the influence of temperature on the reaction chemistry. In all cases, varying proportions of dimethyl carbonate (DMC), dimethoxy methane (DMM), and methyl formate (MeFOR) were produced. When the acetate salts were employed, a fourth product, methyl acetate (MeAc), was also observed as seen from Figure 2. The product distributions present at the end of each experimental trial are given in Figure 3.
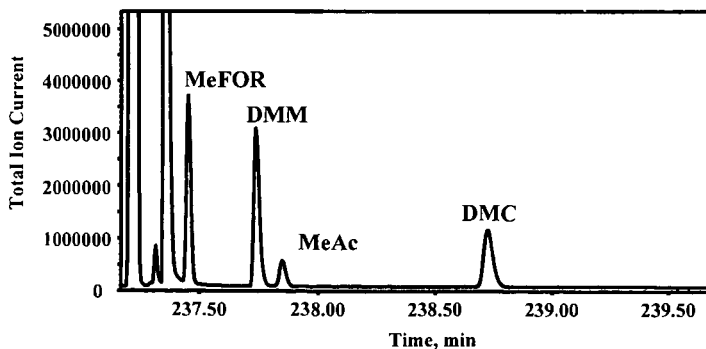

Figure 2. Chromatogram of the products from the following reaction: 0.5 g $CuAc_2$ catalyst, 5.0 g MeOH, 50 psi CO, 100 psi air, 170 °C .
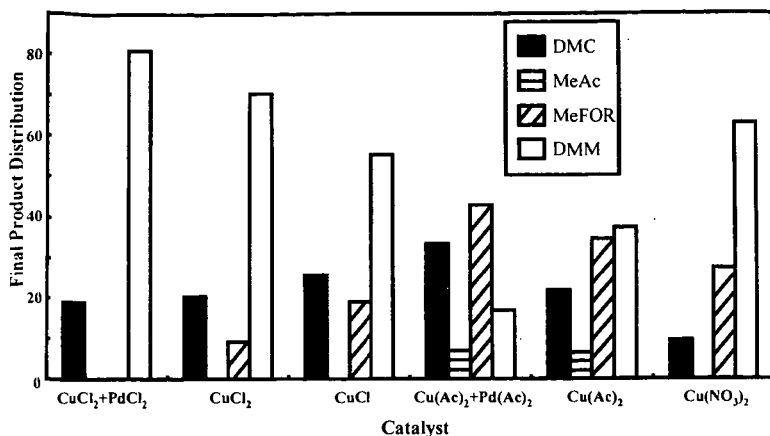
Figure 3. Final product distributions from six different catalysts. All reactions performed under the following conditions: 0.5 g catalyst, 5.0 g MeOH, 50 psi CO, 100 psi air, temperature programmed from 100 °C to 170 °C in 30 min. / 10 °C steps.

Palladium catalyzes the reaction of CO and O_2 to produce a large amount of CO_2, thereby reducing the amount of CO available for the production of DMC. The catalysts with acetate show significant activity, but because of the formation of a fourth product, methyl acetate, we chose the catalysts based on chloride salts for further study. The $Cu(NO_3)_2$ catalyst has the worst selectivity for DMC.

The reactant gas ratio influence was investigated with the CuCl catalyst by using differing amount of CO and air, but maintaining the same total pressure to minimize any pressure effects. Three different gas ratios were used and the product distributions are shown in Figure 4.
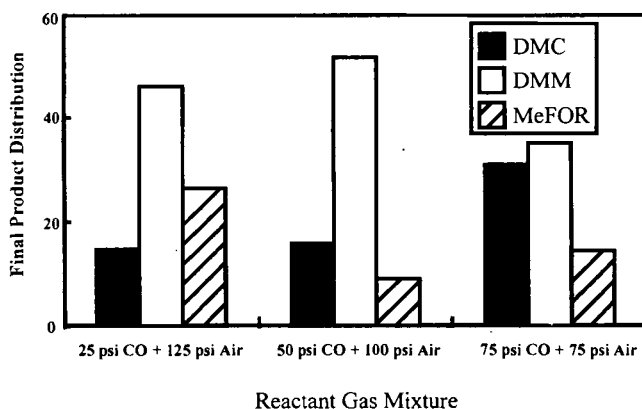

Reactant Gas Mixture

Figure 4. Final product distributions using CuCl catalyst with varying reactant gas ratios.

The influence of the support particle size was examined by using both the $CuCl_2$ and CuCl catalysts on three different activated carbon support sizes. The final peak areas were normalized by dividing the peak area of each reaction product by the peak area of the internal standard, n-hexane. The Tables 1 and 2 show the results.

Table 1. Final Peak Area Ratios using $CuCl_2$ Catalysts

Mesh	DMC Area Ratio	DMM Area Ratio	MeFOR Area Ratio
4-14	0.7255	0.3647	0.9506
20-40	0.5784	1.715	0.3207
100	0.6982	0.4843	1.002

Table 2. Final Peak Area Ratios using CuCl Catalysts			
Mesh	DMC Area Ratio	DMM Area Ratio	MeFOR Area Ratio
4-14	1.025	0.3724	1.008
20-40	0.8210	1.328	0.7746
100	0.7483	0.3387	0.7420
20-40 crush	0.8629	1.278	0.8092

Because no clear trend was evident from the first six experiments, the final experiment was conducted using the 20-40 mesh CuCl catalyst that had been crushed into a fine powder. The results indicate that using the 20-40 mesh catalyst, in both forms, leads to the production of a much larger amount of DMM than either the larger or the smaller support. This evidence led us to conclude that the 20-40 mesh catalysts were causing the reaction of DMC to form DMM. This hypothesis was tested by loading the reactor with a 10 wt. % solution of pure DMC in methanol, $CuCl_2$ catalyst on 20-40 mesh support, and oxygen (from air). Figure 5 represents the results from that experiment.
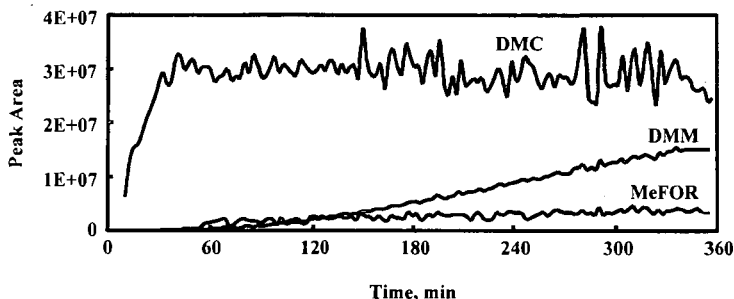

Figure 5. 10 wt. % DMC in methanol and CuCl catalyst.

DMM did gradually appear, but the signal from DMC did not decrease as predicted. The source of the DMM was not the oxidation of DMC, but an independent process. This was tested by charging the autoclave with $CuCl_2$ catalyst on 20-40 mesh, methanol, and oxygen (from air). No CO was added to inhibit the formation of DMC. Figure 6 is the result from that experiment.
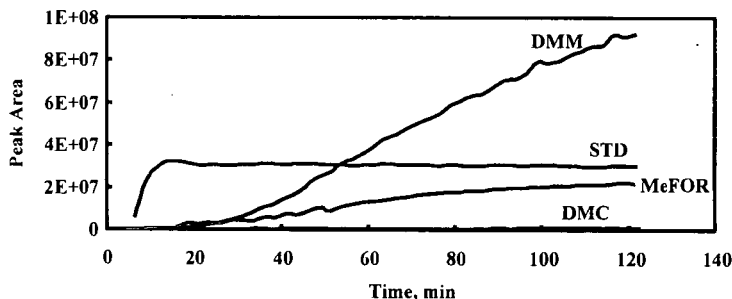

Figure 6. Methanol, $CuCl_2$ catalyst, and air reacting to form DMM.

Only DMM and MeFOR, the two unwanted products, were formed and at nearly the same rate as in a previous experiment in which CO was added.

CONCLUSIONS

The reaction that forms DMM and MeFOR is independent of the reaction that forms DMC. It should be possible to find a different catalyst that is much more selective for DMC due to these uncoupled reactions. From the Tables, it is clear that $CuCl_2$ and CuCl give rise to very similar product distributions. This leads us to conclude that the Cu^+ ion is most likely being oxidized to Cu^{2+} by the O_2 present inside the reactor. Neither the Cu^+ nor the Cu^{2+} catalyst offers a significant advantage over the other. The relationship between support particle size and reactivity appears to be more complicated than originally expected. This phenomenon is currently under investigation.

REFERENCES

1. Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. *Environ. Sci. Technol.,* **1999,** *33,* 318-328.

2. Gouli, S.; Lois, E.; Stournas, S. *Energy & Fuels,* **1998,** *12,* 918-924.

3. Pacheco, M. A.; Marshall, C. L. *Energy & Fuels,* **1997,** *11,* 2-29.

4. Japanese Patent 61[1986]-207496; Imoura, S.; Matsushita, D. "Fuel for Internal Combustion Engine": assigned to Toyo Soda Industry; **1986.**

5. Stoner, M.; Litzinger, T. "Effects of Structure and Boiling Point of Oxygenated Blending Compounds in Reducing Diesel Emissions"; SAE Technical Paper Series; **1999;** 1999-01-1475.

6. Murayama, T.; Zheng, M.; Takemi, C.; Oh, Y.; Fujiwara, Y.; Tosaka, S.; Yamashita, M.; Yoshitake, H. "Simultaneous Reductions of Smoke and Nox from a DI Diesel Engine with EGR and Dimethyl Carbonate"; SAE Technical Paper Series; **1995;** 952518.

7. US Patent 4,891,049; Dillon, D. M.; Iwamoto, R. Y. "Hydrocarbon Fuel Composition Containing Carbonate Additive"; assigned to Unocal; **1990.**

8. US Patent 4,904,279; Kanne, D. M.; Iwamoto, R. Y. "Hydrocarbon Fuel Composition Containing Carbonate and Dicarbonate Additives"; assigned to Union Oil; **1990.**

9. US Patent 5,902,894; Ryu, J. Y. "Process for Making Dialkyl Carbonates"; assigned to Catalytic Distillation Technologies; **1999.**

10. Sakakura, T.; Saito, Y.; Okano, M.; Choi, J.; Sako, T. *J. Org. Chem.,* **1998,** *63,* 7095-7096.

11. Cheong, M.; Kim, S.; Park, J. *New J. Chem.,* **1997,** *21,* 1143-1145.

12. Tomishige, K.; Sakaihori, T.; Ikeda, Y.; Fujimoto, K. *Cat. Lett.,* **1999,** *58,* 225-229.

13. Matsuzaki, T.; Ohdan, K.; Asano, M.; Tanaka, S.; Nishihira, K.; Chiba, Y. *J. Chem. Soc. Japan,* **1999,** 15-24.

14. Yanji, W.; Xinqiang, Z.; Baoguo, Y.; Bingchang, Z.; Jinsheng, C. *Applied Catalysis, A: General,* **1998,** *171,* 255-260.

15. Tomishige, K.; Sakaihori, T.; Sakai, S.; Fujimoto, K. *Applied Catalysis, A: General,* **1999,** *181,* 95-102.

16. Meuzelaar, H.L.C. "Comparison of On-line MS Techniques for Complex Reactive Systems," *Proceedings of the Specialists Workshop on Applications of Free-Jet Molecular Beam, Mass Spectrometric Sampling,* October 12-14, Estes Park Center, CO, NTIS, **1994,** NREL-CP-433-7748, 57-64.

17. Meuzelaar, H.L.C.; Liu, K.; Jakab, E. "Development of On-Line Chemical Speciation and Microsimulation Techniques for High Pressure Conversion Reactions in Coals & Waste Materials," *Proceedings of the 1994 U.S. Dept. of Energy Coal Liquefaction and Gas Conversion Contractors' Review Conference,* September 7-8, Pittsburgh, PA, **1994,** 637-649.

18. Nie, X.; McClennen, W.H.; Liu, K.; Meuzelaar, H.L.C. "Development of On-Line GC/MS Monitoring Techniques for High Pressure Fuel Conversion Processes," *ACS Preprints, Division of Fuel Chemistry,* **1993,** 38 (4), 1147-1155.

19. Arnold, N.S.; McClennen, W.H.; Meuzelaar, H.L.C. "Vapor Sampling Device for Rapid Direct Short Column Gas Chromatography/Mass Spectrometry Analyses of Atmospheric Vapors," *Analytical Chemistry,* **1991,** 63, 299-304.